Coverage Effect of the CO2 Adsorption Mechanisms on CeO2(111) by First Principles Analysis

Hahn, Konstanze R ; Iannuzzi, Marcella ; Seitsonen, Ari P ; Hutter, Juerg

Abstract: The adsorption of carbon dioxide on CeO2(111) has been studied using density functional theory. At low coverage (1/9 monolayer), CO2 is found to preferably adsorb in a monodentate configuration forming a carbonate species with a surface O atom. In this configuration, the CO2 molecule is bent with an O-C-O angle of 129 degrees and a remarkable elongation (to 1.27 angstrom) of the C-O bond length compared to the gas phase molecule, indicating a high degree of CO2 activation. A similar activation is observed when the CO2 molecule adsorbs as bidentate carbonate; however, this configuration is less stable. Linear configurations are found to adsorb very weakly at low coverage by physisorption. Increasing the coverage leads to a decrease of the stability of mono- and bidentate configurations which can be attributed to repulsive interactions between adjacent adsorbates and the limited capacity of the CeO2(111) surface to donate electrons to the adsorbates. In contrast, the binding energy of linearly adsorbed CO2 is shown to be coverage independent. At coverages >1/4 monolayer, we have also addressed the stability of mixed configurations where monodentate, bidentate, and linear species are present simultaneously on the surface. The most stable configurations are found when 1/3 monolayer CO2 is bound as monodentate species, and additional molecules are physisorbed forming partial layers of linear species. Analysis of the projected density of states has shown that the orbitals of linear species in the first partial layer lie at lower energies than the ones of the second partial layer suggesting stabilization of the former through interactions with preadsorbed monodentate species. These findings provide fundamental insight into the CO2 adsorption mechanism on CeO2 and potentially assist the design of new Ce-based materials for CO2 catalysis.

DOI: https://doi.org/10.1021/jp309565u

Coverage effect of the CO_2 adsorption mechanisms on CeO_2(111) by first principles analysis

*Konstanze R. Hahn, Marcella Iannuzzi, Ari P. Seitsonen, Jürg Hutter**

Supporting Information

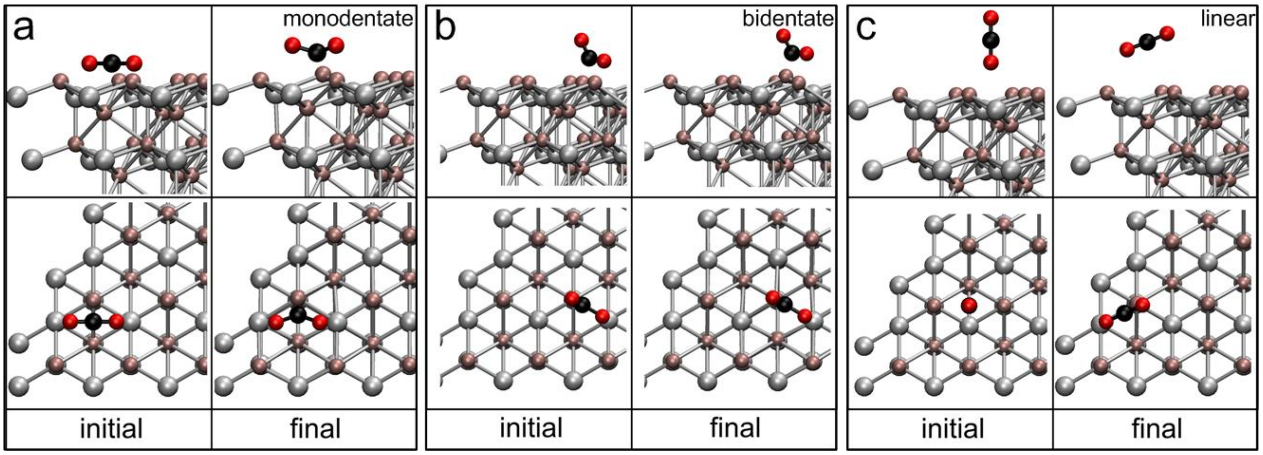

Figure S1. Initial and final configurations for stable configurations of CO_2 on CeO_2(111). When the linear CO_2 molecule was initially placed close to the surface (1.7 Å), the molecule spontaneously bent to form a monodentate species (a).

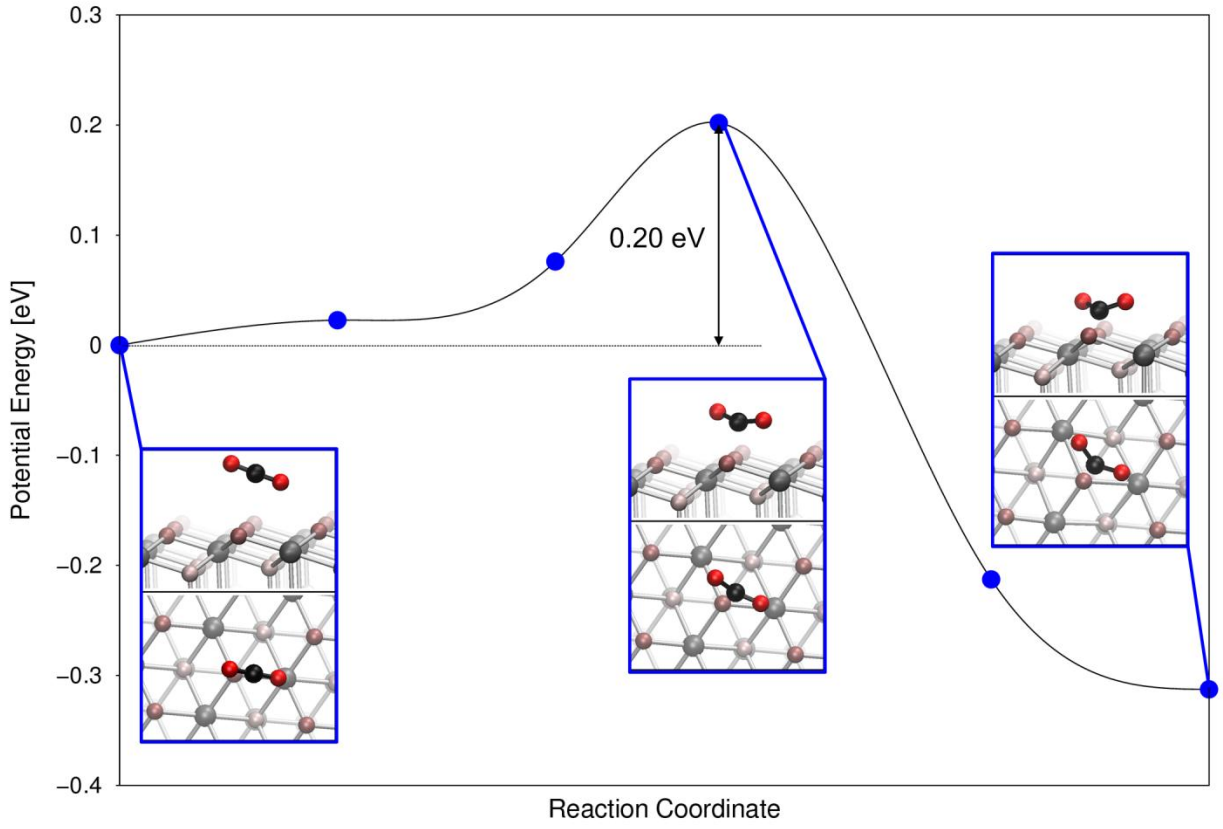

Figure S2. Potential energy surface for the transition of the linear to the monodentate configuration of CO_2 obtained from nudge elastic band calculations. For the adsorption of CO_2 in the bent monodentate configuration, an activation energy of 0.2 eV is determined. In the transition state the O-C-O angle decreases to 152.1° and the C-O bond length elongates to 1.20 Å.

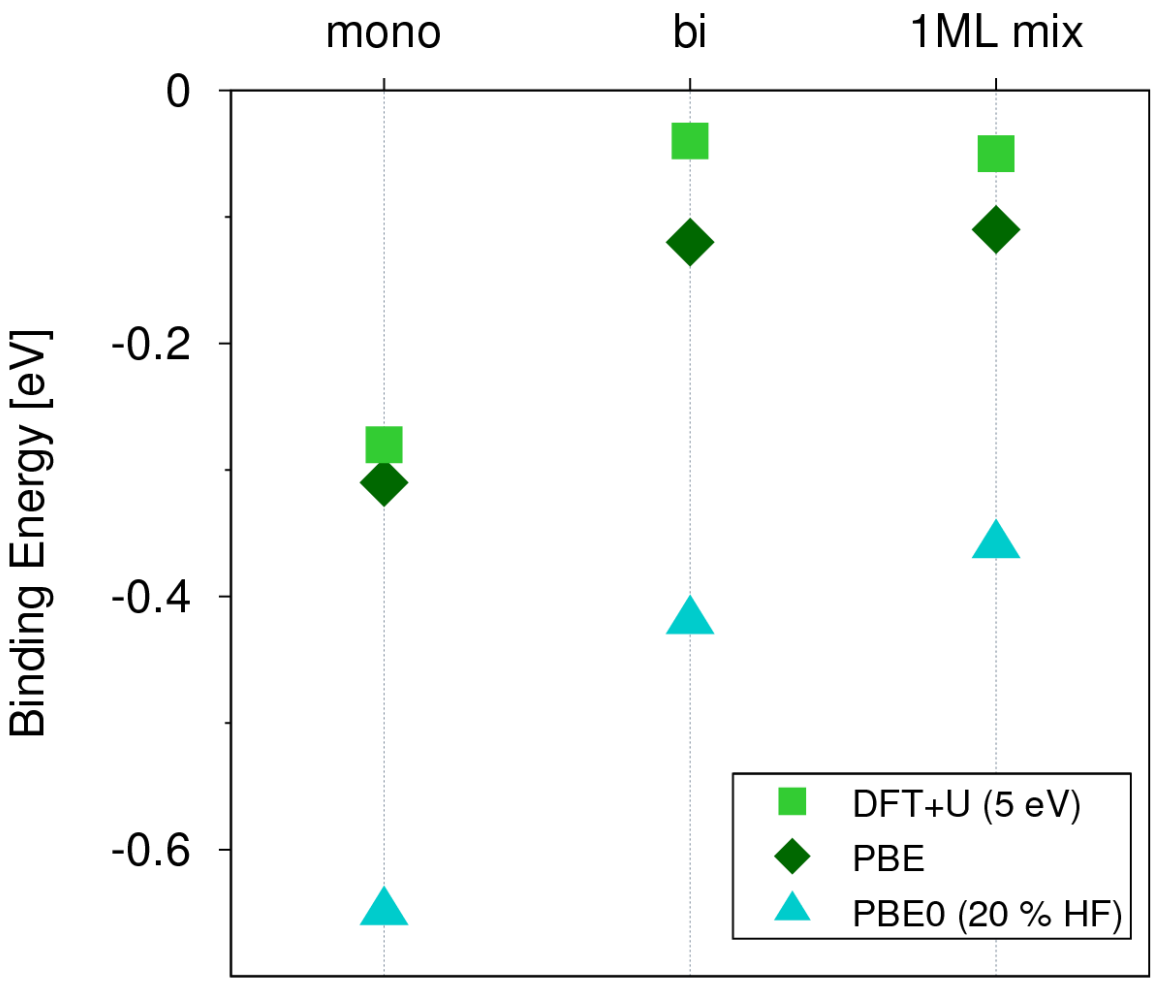

Figure S3. Binding energy of selected configurations (mono- and bidentate at 1/9 ML and mixed configuration of monodentate and linear species at 1 ML) of CO_2 adsorbed on CeO_2(111) calculated with DFT+U (U=5 eV) (squares), standard DFT using the PBE functional (diamonds) and PBE0 (triangles). Spin-polarization was considered in PBE0 calculations. PBE0 calculations were performed using 20% exact exchange. All methods show the same trends for the stability of different adsorption mechanisms.

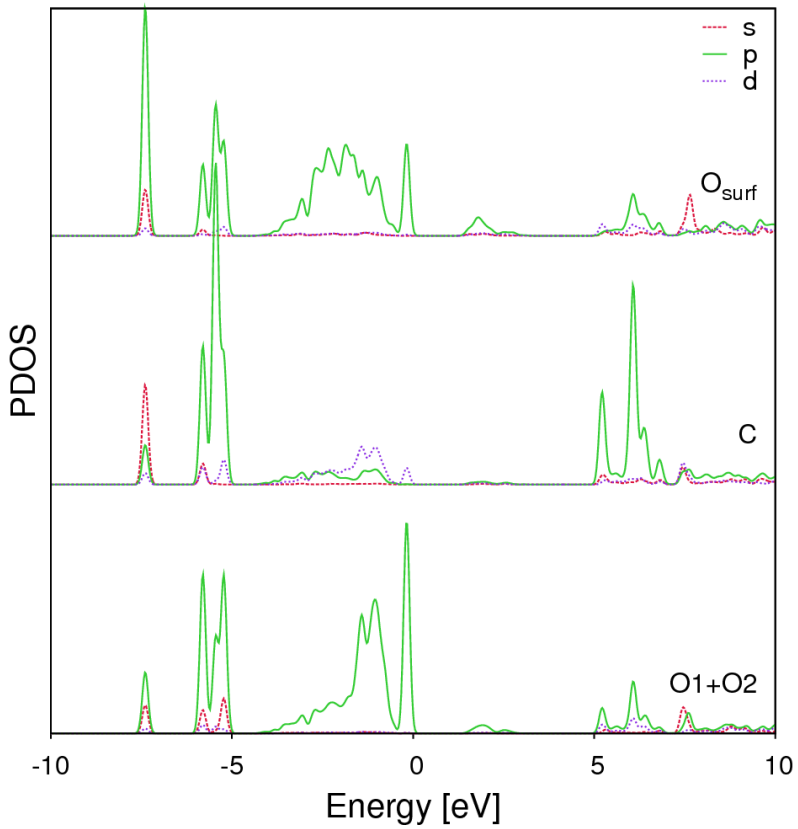

Figure S4. PDOS on s- (red lines), p- (green lines) and d-type (violet lines) orbitals of the O_{surf} atom and the C and O (O_{CO2}) atoms of the CO_2 molecule adsorbed on CeO_2(111) in a monodenate configuration at 1/9 ML coverage. Binding of the CO_2 molecule at the valence band to the O_{surf} atom takes place through p-orbitals of the O atoms and hybridized orbitals of the C atom with d-character.

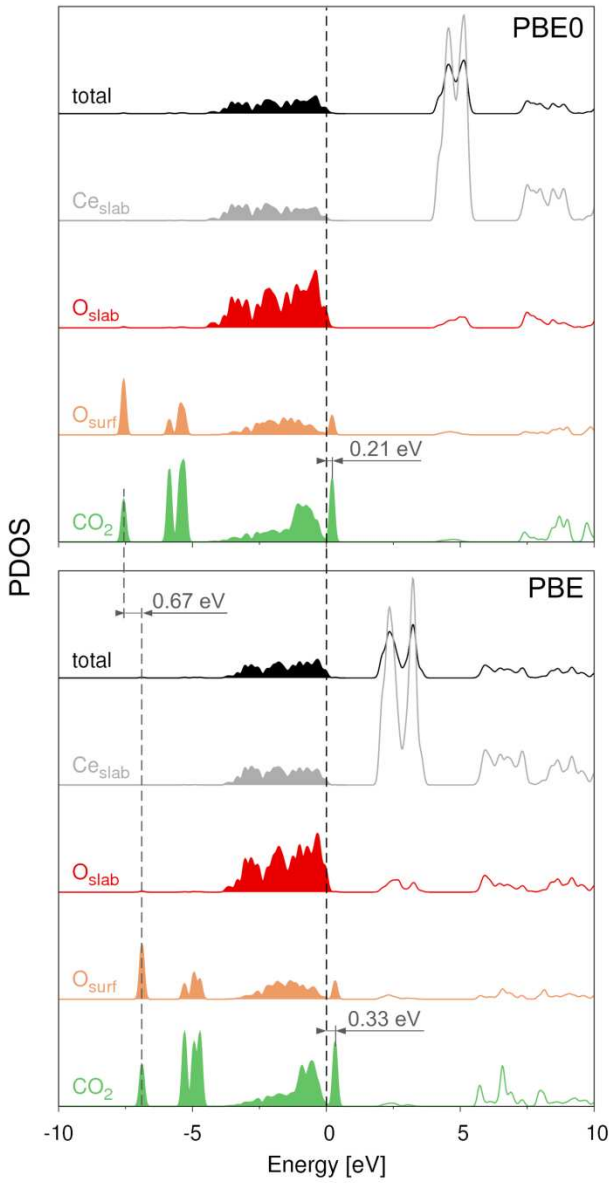

Figure S5. PDOS summed over all atoms (black) and on specific species (Ce_{slab}, O_{slab} and CO_2) of isolated (1/9 ML) CO_2 adsorbed on CeO_2(111) in a monodentate configuration calculated with PBE0 (top) and standard DFT (PBE, bottom). CO_2 orbitals ca. 6 eV below the valence band are shifted to lower energies (by ca. 0.67 eV) when PBE0 was used. Additional CO_2 states are found at 0.21 and 0.33 eV above the valence band for PBE0 and PBE calculations, respectively.

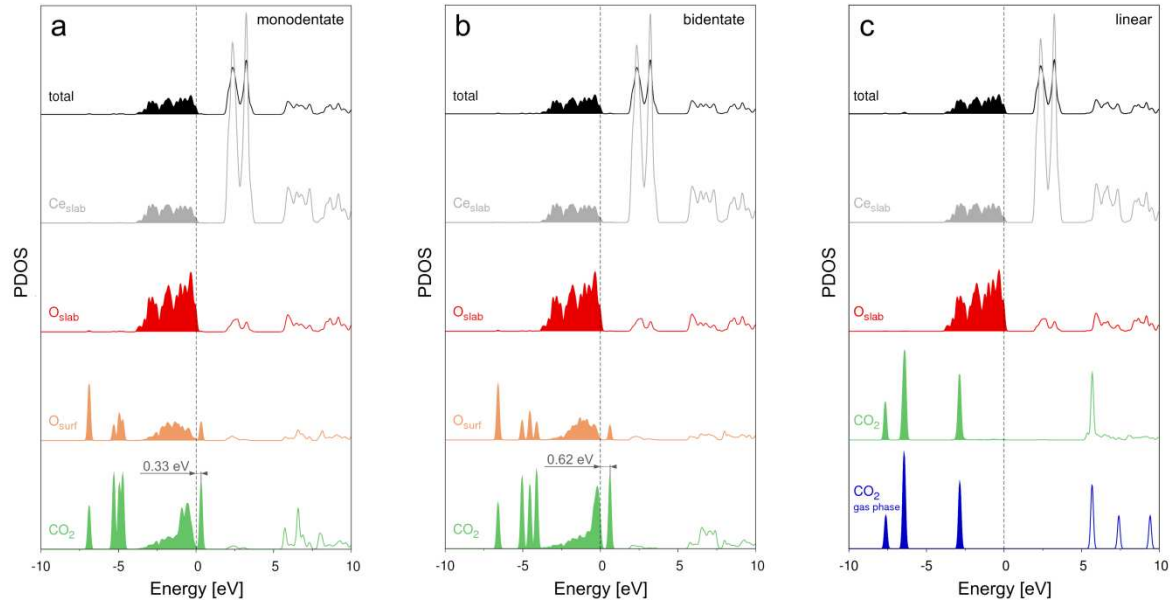

Figure S6. Total (black lines) and projected DOS on the orbitals of substrate Ce (Ce_{slab}, grey lines) and O (O_{slab}, red lines) atoms upon adsorption of CO_2 (green lines) as (a) monodentate, (b) bidentate and (c) linear species. In the case of linear adsorption, additionally the DOS of linear CO_2 in the gas phase (blue line) is shown, where the energy levels have been shifted to match the energy levels of linear CO_2 physisorbed on CeO_2(111). The reference 0 eV has been set to the valence band of the CeO_2 substrate. One additional state evolves above the valence band of CeO_2 in the case of mono- and bidentate CO_2 adsorption. This can be attributed to the hybridized HOMO of gas phase CO_2 and lies 0.33 and 0.62 eV above the CeO_2 valence band in the mono- and bidentate configuration, respectively.

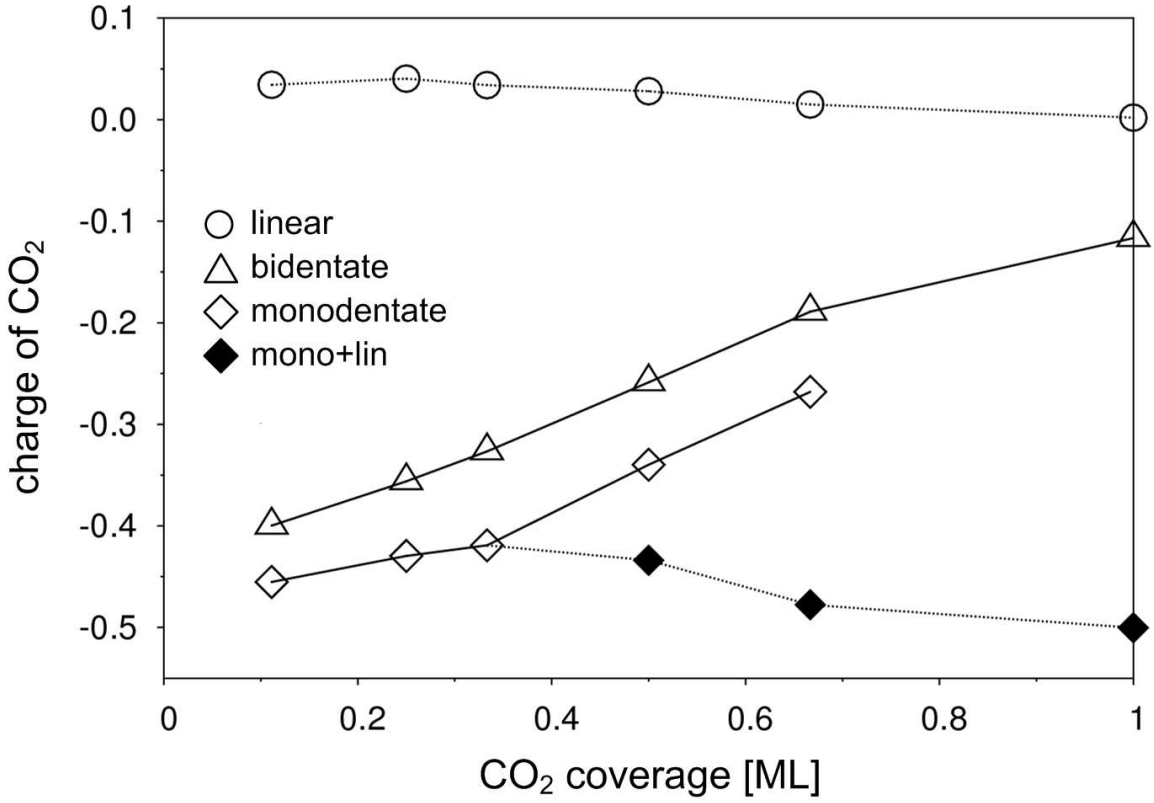

Figure S7. Average charge per CO_2 molecule adsorbed linearly (circles), as bidentate (triangles) and monodentate (diamonds) species as a function of the CO_2 coverage. Filled diamonds show the charge of monodentate species (1/3 ML) when additional CO_2 is adsorbed as linear species. In this case, the charge of the monodentate species even decreased slightly with increasing amount of linear CO_2 indicating an additional charge transfer from linear to monodentate CO_2 species.